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# STRUCTURAL DEPENDENCIES OF PYRAMIDAL INVERSION AT SULPHUR AND SELENIUM IN THIO- AND SELENO- ETHER COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

## A NUCLEAR MAGNETIC RESONANCE STUDY

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**Abstract**—Total NMR band shape fitting methods have provided accurate energy data for inversion barriers at sulphur and selenium in complexes of types *cis*-$[MX_2L]$ ($M = Pd^{II}, Pt^{II}$; $X = Cl, Br, I$; $L = MeS(CH_2)_2SMe$, $MeS(CH_2)_3SMe$, o-$(SMe)_2C_6H_3Me$, *cis*-MeSCH=CHSMe) and $[PtXMe\{MeE(CH_2)_2E'Me\}]$ ($E = E' = S$ or Se and $E = S, E' = Se$; $X = Cl, Br, I$). Barrier energies were found to decrease by 10–12 kJ mol$^{-1}$ in going from aliphatic through aromatic to olefinic ligand back-bone. This can be explained in terms of $(3p - 2p)\pi$ conjugation between the inverting centre and the ligand back-bone. The effects of ligand ring size, nature of halogen atom and the metal oxidation state on the barrier energies are discussed.

### INTRODUCTION

The use of the NMR technique for studying sulphur inversion dates back to 1966 when Abel *et al.*[1] examined the Pt(II) chelate $[PtCl_2\{MeS(CH_2)_2SMe\}]$. Shortly afterwards, Haake and Turley[2,3] examined the effect of *trans* influence on inversion rates in complexes *cis* and *trans*-$[PtCl_2(SRR')_2]$ (R = Me, Et, Bz). More recently, Cross *et al.*[4–7] and Hunter *et al.*[8–10] have studied S, Se and Te inversion in a wide range of Pd(II) and Pt(II) complexes. Energy barriers to inversion were, in most cases, based only on coalescence temperature measurements in contrast to our own studies which utilised total band shape analysis. This method has been rigorously applied to the Pd(II) and Pt(II) complexes $[MX_2\{ER(CH_2SiMe)\}_2]$ ($E = S$, Se; $R = CH_2SiMe_3$, Me, Ph)[11,12] and $[MX_2\{\overline{S(C}R_2)_n\}_2]$ (R = H and/or Me; $n = 2$–5).[13,14] Latterly, however, we have been examining chalcogen inversion in Pt(IV) complexes, in particular $[PtXMe_3\{MeE(CH_2)_nE'Me\}]$ ($E = E' = S$ or Se, $n = 2, 3$)[15] and ($E = S$, $E' = Se$, $n = 2, 3$).[16] Since little is known about the influence of the oxidation state of platinum on the inversion rates of S and Se we have now prepared and examined Pt(II) complexes of general type $[PtXMe\{MeE(CH_2)_2EMe\}]$ ($X = Cl, Br, I$; $E = S$, Se, S/Se). Furthermore, in order to examine whether the chalcogen inversion rates depend on the electronic nature of the ligand back-bone, we have prepared the following complexes with aliphatic, aromatic and olefinic back-bones, *cis*-$[MX_2L]$($M = Pd(II)$, Pt(II); $X = Cl$, Br, I; $L = MeS(CH_2)_2SMe$, $MeS(CH_2)_3SMe$, o-$(SMe)_2C_6H_3Me$ and *cis*-MeSCH = CHSMe). Some of the complexes have been reported previously[4,5,17] but only limited inversion studies have been carried out. We report here accurate inversion energy data and discuss the major structural dependencies of these values.

### EXPERIMENTAL

*Materials*. The ligands 1,3-bis(methylthio)propane, 1,2-bis(methylthio)ethane and *cis*-1,2-bis(methylthio)ethene were prepared by previously reported methods.[17] 3,4-Bis(methylthio)toluene was prepared by the methylation of toluene-3,4-dithiol (B.D.H.). 1,2-Bis(methylthio)benzene was isolated by the methylation of o-methylthiobenzene thiol.[18]

Preparations of complexes of the above ligands were based on standard general methods[19] with some improvements. A typical preparation was as follows. Potassium tetrachloroplatinate(II) (0.5 mmol) and the ligand (1.0 mmol) were refluxed in an ethanol/water (3:1) mixture for *ca.* 12 hr. The resulting precipitate was filtered, washed with water and ethanol, and further purified by recrystallisation from a suitable solvent depending on the ligand as follows: 3,4-bis(methylthio)toluene (dichloromethane or chloroform), 1,2-bis(methylthio)propane (acetonitrile), 1,2-bis(methylthio) ethane and 1,2-bis(methylthio)ethene (Soxhlet extraction using ethanol or dichloromethane as solvent).

The corresponding dibromide and diiodide complexes were prepared by refluxing the dichloride complex with lithium bromide or iodide in ethanolic solution.

The ligands 1,2-bis(methylseleno)ethane (b.p. 88°C/8 mmHg) and 1-methylthio-2-methylselenoethane (b.p. 82°C/10 mmHg) were prepared by literature methods.[20,16]

[*Chloro*(*methyl*) ($\eta^4$-*1,5-cyclooctadiene*)*platinum*(*II*)]. (m.p. 166–167°C) was prepared from [dimethyl($\eta^4$-1,5-cyclooctadiene)platinum(II)].[21] The corresponding bromo- and iodo-complexes were obtained by adding excess of the appropriate potassium halide to an acetone solution of the chloro compound. Immediate precipitation was noted (white–bromide, yellow–iodide). After stirring for 1 hr, acetone was removed by rotary evaporation. The residue was collected on a frit, washed with distilled water followed by pentane and air dried (90–95°C) to give either white [*bromo*(*methyl*) ($\eta^4$-*1,5-cyclooctadiene*)*platinum*(*II*)], m.p. 170–171°C, or yellow [iodo(methyl) ($\eta^4$-1,5-cyclooctadiene)platinum(II)], m.p. 139–140°C.

The preparations of the complexes $[PtXMe\{MeE(CH_2)_2E'Me\}]$ were very similar, and only a representative method for one of the chloride complexes is given. An excess of 1-methylthio-2-methylseleno-ethane (0.1088 g; 0.64 mmol) in chloroform (3 cm$^3$) was added to a solution of [chloro(methyl) ($\eta^4$-1,5-cyclooctadiene)platinum(II)] (0.2114 g; 0.599 mmol) in chloroform (5 cm$^3$). After refluxing for 2 hr the solvent was removed. Recrystallisation from dichloromethane/hexane gave [*chloro*(*methyl*)(*1 - methylthio - 2 - methylselenoethane*)*platinum*(*II*)] as a pale yellow powder (0.141 g; 57%).

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***Spectra.*** All $^1$H NMR spectra (with one exception, see later) were recorded on a JEOL PS/PFT-100 spectrometer operating in the F.T. mode at 100 MHz. Complexes were studied in a variety of solvents (see later). A standard variable temperature unit was used to control the probe temperature. Temperatures were recorded immediately before and after running the spectra and were measured with a copper-constantan thermocouple with an accuracy of ≤1°C. Computer simulations of spectra were achieved with a program based on that of Binsch.[22]

## RESULTS

Analytical data for the complexes are collected in Tables 1 and 2.

### *cis*-[$MX_2L$] complexes

All these five and six membered ring complexes of palladium(II) and platinum(II) possess the same basic geometry and differ only in the ligand back-bone. At

Table 1. Characterisation of the *cis*-[$MX_2L$] complexes

| No. | M | L | X | Colour | M.p/°C | Analysis*/% C | H |
|---|---|---|---|---|---|---|---|
| 1 | Pt | $MeSC_2H_4SMe$ | Cl | Pale yellow | 234 | 12.20 (12.35) | 2.75 (2.60) |
| 2 | | | I | Yellow | 242 | 8.50 (8.40) | 1.65 (1.75) |
| 3 | Pt | $MeSC_2H_2SMe$ | Cl | Yellow | 208(d) | 12.25 (12.40) | 1.10 (1.10) |
| 4 | | | I | Dark yellow | 189(d) | 8.65 (8.45) | 1.40 (1.40) |
| 5 | Pt | o-$(SMe)_2C_6H_3Me$ | Cl | Yellow | 230 | 23.85 (24.00) | 2.50 (2.65) |
| 6 | | | Br | Orange-yellow | 260(d) | 20.30 (20.05) | 2.10 (2.20) |
| 7 | | | I | Dark yellow | 235(d) | 17.35 (17.10) | 1.80 (1.90) |
| 8 | Pt | $MeSC_3H_6SMe$ | Cl | Pale yellow | 239 | 14.80 (14.95) | 2.95 (3.00) |
| 9 | Pd | $MeSC_2H_4SMe$ | Cl | Dark yellow | 242(d) | 15.75 (16.00) | 3.45 (3.35) |
| 10 | | | I | Purple | 215(d) | 10.00 (9.95) | 2.00 (2.05) |
| 11 | Pd | $MeSC_2H_2SMe$ | Cl | Light yellow | 192 | 14.85 (16.05) | 2.70 (2.70) |
| 12 | | | I | Dark red | 175(d) | 10.00 (10.00) | 1.65 (1.65) |
| 13 | Pd | o-$(SMe)_2C_6H_3Me$ | Cl | Yellow | 240(d) | 29.65 (29.80) | 3.25 (3.30) |
| 14 | | | Br | Dark yellow | 210(d) | 23.90 (23.95) | 2.55 (2.65) |
| 15 | | | I | Purple | 195 | 19.90 (19.85) | 2.05 (2.20) |

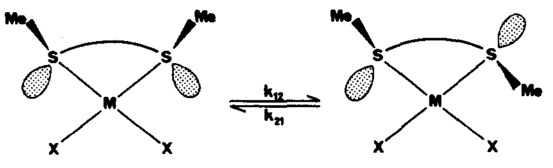
*Calculated values in parentheses

(d) decomposes

Table 2. Characterisation of the *cis*-[PtXMeL] complexes

| No. | L | X | Colour | M.p./°C | Analysis*/% C | H |
|---|---|---|---|---|---|---|
| 16 | $MeSC_2H_4SMe$ | Cl | White | 152 - 154 | 16.00 (16.35) | 3.50 (3.55) |
| 17 | | Br | Pale yellow | 136 - 137 | 14.95 (14.55) | 3.00 (3.15) |
| 18 | | I | Yellow | 133 - 135 | 12.90 (13.10) | 2.70 (2.85) |
| 19 | $MeSeC_2H_4SeMe$ | Cl | Light orange | 144 - 146 | 12.85 (13.00) | 2.80 (2.80) |
| 20 | | Br | Orange | 141 - 142 | 11.55 (12.20) | 2.40 (2.65) |
| 21 | | I | Dark orange | 137 - 138 | 10.85 (11.15) | 2.20 (2.40) |
| 22 | $MeSC_2H_4SeMe$ | Cl | Pale yellow | 139 - 140 | 14.55 (14.50) | 3.10 (3.15) |
| 23 | | Br | Pale yellow | 144 - 146 | 13.25 (13.05) | 2.80 (2.85) |
| 24 | | I | Orange-yellow | 132 - 133 | 11.60 (11.85) | 2.45 (2.55) |

*Calculated values in parentheses



meso
(1)

dl
(2)

Fig. 1. Diastereoisomers of *cis*-[$MX_2L$] (L = homochalcogen ligands with aliphatic, aromatic or olefinic backbones) complexes.

ambient (Pt complexes) or lower temperatures (Pd complexes) the $^1H$ spectra were consistent with the presence of two diastereoisomers, *meso* and DL, generally in unequal abundances (Fig. 1) (Table 3). This is strikingly apparent in the 360 MHz spectrum of [$PdI_2${*o*-$(SMe)_2C_6H_3Me$}] at −70°C (Fig. 2), where isomeric distinction is clearly observed in the –SMe, the –CMe and the three aromatic proton signals.

On warming the complexes in solution the spectra change in accord with an increasing rate of sulphur inversion such that at higher temperatures (*ca.* 60°C) time-averaged signals for the two isomers were observed. These changes were fully consistent with previous qualitative studies on certain of these complexes.[1,15,17] In order to evaluate the sulphur inversion barriers accurately in all the present complexes, we chose to study the band shape changes of the methyl and (where appropriate) olefinic protons. The spectra of [$PtCl_2$(MeSCH=CHSMe)] may be taken as typical (Fig. 3). At low temperatures the two olefinic signals for the *meso* and DL isomers (plus $^{195}Pt$ satellites) are clearly visible as sharp singlets. On raising the temperature, coalescence of the signals occurs, which is complete by *ca.* 60°C. Computation of the energy barrier for the inversion process was straightforwardly accomplished using the static parameters in Table 3 and the authors' version of the standard band shape program[22] for the spin problem

$$\underset{66.3\%}{\underset{(\text{meso})\ (\text{DL})}{A \rightleftharpoons B}} \qquad \underset{33.7\%}{\underset{(\text{meso})\ (\text{DL})}{AX \rightleftharpoons BX}} \qquad X = {}^{195}\text{Pt}$$

Table 3. Static parameters used in the computations of the SMe signals of *cis*[$MX_2L$] complexes

| Complex No. | T/°C | Meso (syn) isomer | | | DL (anti) isomer | | | $T_2^*$/s |
|---|---|---|---|---|---|---|---|---|
| | | $\nu_A$[a]/Hz | $^3J$(PtH)/Hz | $p_1$[b] | $\nu_B$[a]/Hz | $^3J$(PtH)Hz | $p_2$[b] | |
| 1 | 54.0 | 271.7 | 48.3 | 0.44 | 259.6 | 49.3 | 0.56 | 0.320<br>0.240[c] |
| 2 | 27.0 | 286.9 | 51.3 | 0.30 | 259.3 | 50.5 | 0.70 | 0.230 |
| 3 | -11.3 | 287.4<br>679.0[d] | 48.0<br>82.5 | 0.40<br>0.40 | 280.8<br>668.0 | 43.6<br>77.8 | 0.60<br>0.60 | 0.330<br>0.330 |
| 4 | -25.8 | 296.4<br>654.8[d] | 51.0<br>78.9 | 0.47<br>0.46 | 299.8<br>643.8 | 45.4<br>73.8 | 0.53<br>0.54 | 0.270<br>0.270 |
| 5 | 11.7 | 311.6<br>308.6 | 47.1<br>46.8 | 0.39<br>0.39 | 305.4<br>302.5 | 45.8<br>45.9 | 0.61<br>0.61 | 0.455[2] |
| 6 | -5.5 | 305.4<br>301.4 | 49.0<br>47.9 | 0.47<br>0.47 | 303.2<br>299.1 | 48.7<br>47.9 | 0.53<br>0.53 | 0.382<br>0.382 |
| 7 | -38.6 | 315.2<br>312.6 | 48.3<br>48.7 | 0.50<br>0.50 | 312.6<br>310.3 | 48.7<br>49.2 | 0.50<br>0.50 | 0.286<br>0.208[c] |
| 8 | -1.9 | 270.0 | 45.4 | 0.49 | 262.9 | 48.1 | 0.51 | 0.180 |
| 9 | 1.8 | 266.4 | - | 0.50 | 259.3 | - | 0.50 | 0.340 |
| 10 | -10.0 | 282.9 | - | 0.36 | 261.3 | - | 0.64 | 0.185 |
| 11 | -32.8 | 284.4<br>672.4[d] | -<br>- | 0.23<br>0.23 | 275.5<br>662.6 | -<br>- | 0.77<br>0.77 | 0.327<br>0.360 |
| 12 | -74.0 | 310.8<br>694.0[d] | -<br>- | 0.32<br>0.32 | 317.1<br>683.9 | -<br>- | 0.68<br>0.68 | 0.250<br>0.320 |
| 13 | -36.2 | 304.7<br>302.5 | -<br>- | 0.41<br>0.41 | 299.8<br>297.6 | -<br>- | 0.59<br>0.59 | 0.509[e]<br>0.509[e] |
| 14 | -68.0 | 309.2<br>307.7 | - | 0.43<br>0.43 | 307.7<br>305.8 | - | 0.57<br>0.57 | n<br>n |
| 15 | -70.0 | 311.8<br>309.4 | - | 0.47<br>0.47 | 317.0<br>314.6 | | 0.53<br>0.53 | 0.187[e]<br>0.187[e] |

[a] Shifts measured at 100 MHz relative to $Me_4Si$

[b] Populations accurate to ± 0.005

[c] For $^{195}Pt$ satellite lines

[d] Olefinic protons

[e] Slightly temperature dependent

[n] Not measured

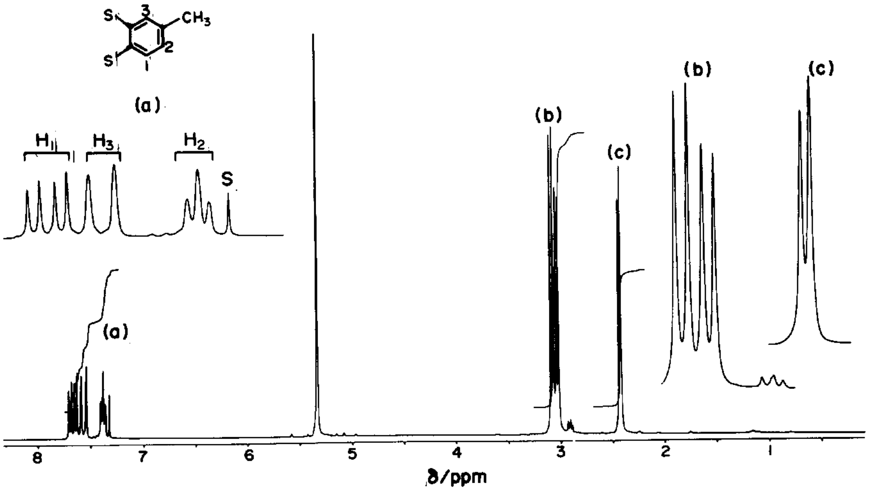


Fig. 2. 360 MHz $^1$H spectrum at $-70$°C of $[PdI_2\{o\text{-}(SMe)_2C_6H_3Me\}]$ in $CD_2Cl_2$ showing isomeric distinction in (a) the aromatic, (b) the -SMe and (c) the -CMe regions. In the aromatic region $J_{12} = 7.5$ and $J_{23} \approx 2$ Hz.

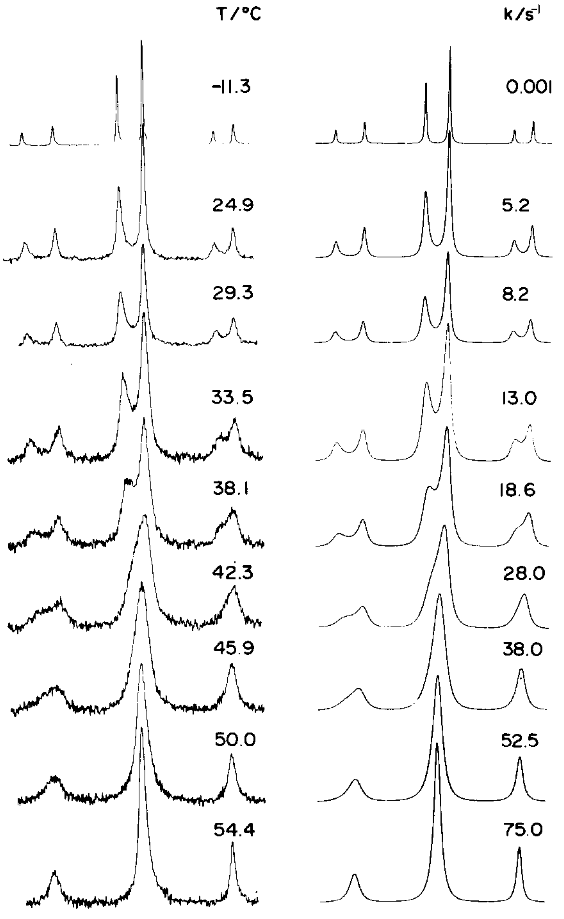


Fig. 3. Experimental and theoretical 100 MHz $^1$H spectra of the olefinic region of $[PtCl_2\,(MeSCH{=}CHSMe)]$ showing the effects of pyramidal S inversion.

Activation parameters for the inversion process were calculated from the usual Arrhenius and Eyring plots (Fig. 4) and are reported in Table 4. The errors quoted are standard deviations, those for $\Delta G^{\neq}$ being quoted in the manner recommended by Binsch.[23] The energies are, in all cases, based on the rate constants $k_{12}$ for the interconversion *meso* → DL. For the complexes with olefinic back-bone $[MX_2(MeSCH{=}CHSMe)]$, the band shape changes in both the SMe and -CH=CH- regions were computed. The two energies subsequently calculated were in excellent agreement (Table 4).

### *cis*-[*PtXMeL*] *complexes*

In the complexes ($L = MeS(CH_2)_2SMe$ or $MeSe(CH_2)_2SeMe$) the chalcogen atoms are centres of chirality and thus, in the absence of any internal exchange process, two diastereoisomers may exist, one with *syn* chalcogen methyls and the other with *anti* chalcogen methyls (Fig. 5). At low temperatures (*ca.* −60°*C*) the spectra showed the presence of both isomers in solution, the more abundant species being attributed to the *anti* conformation (Table 5). Taking the complex $[PtClMe\{MeS(CH_2)_2SMe\}]$ as a representative case, the -SMe region exhibited four signals (plus $^{195}$Pt satellites) at *ca.* −50°C whereas the methylene region was predictably complex. Two PtMe signals (plus $^{195}$Pt satellites) were observed at lower frequencies. Chemical shift and coupling constant data for this and the other complexes have been collected in Table 5. On warming the sample, band broadening commenced and by *ca.* 20°C bands had coalesced and sharpened again to reveal two averaged SMe signals (one each for the SMe groups *trans* to the halogen and methyl groups) and one averaged PtMe signal. The methylene region absorption was still very complex and was not analysed. On heating the complex to its decomposition point, *ca.* 160°C, no further spectral changes were observed. Throughout this temperature range, −60°C to 160°C, $^{195}$Pt-H coupling was retained, confirming the absence of any ligand dissociation.

In these complexes, in contrast to the complexes $[PtX_2\{MeS(CH_2)_2SMe\}]$, sulphur pyramidal inversion can proceed via two different transition states depending on whether the chalcogen *trans* to methyl ($E_1$) or *trans* to chalcogen ($E_2$) inverts (Fig. 5). Since there are only two chemically distinct species *syn* and *anti*, NMR will not be able to distinguish between these two inversion pathways. If, however, the two inversion barrier energies are substantially different (see later), the spectra will be

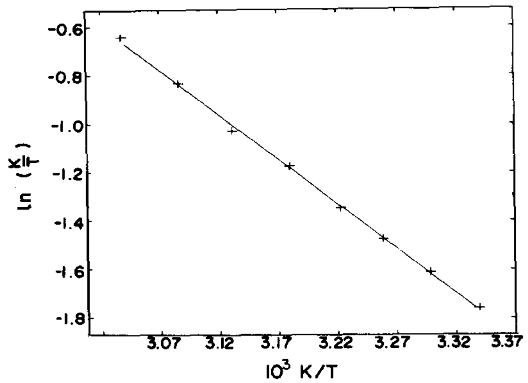


Fig. 4. Eyring plot for the olefinic band fittings of [PtCl$_2$(MeSCH=CHSMe)].

sensitive only to the lower energy process. Studies on [PtX$_2${MeS(CH$_2$)$_2$SMe}] demonstrated band coalescences at *ca.* 100°C as a result of independent inversion of each sulphur atom. The much lower coalescences (*ca.* 0°C) in the [PtXMe{MeS(CH$_2$)$_2$SMe}] complexes imply that the spectral changes here are a consequence of inversion at sulphur *trans* to methyl (E$_1$ in Fig. 5) and are totally insensitive to the (presumably) higher energy inversion of the sulphur *trans* to halogen. Energy barriers for the former process were computed in the usual way and the data are reported in Table 6.

Complexes of this type involving mixed S/Se ligands, e.g. [PtXMe{MeS(CH$_2$)$_2$SeMe}], can exist as two geometrical isomers each of which occurs as a diastereoisomeric DL pair (Fig. 6). Interconversion between these DL pairs takes place by pyramidal inversion at either the sulphur or the selenium atoms. At low temperatures (*ca.* −50°C) the $^1$H spectra clearly indicated the presence of all four DL isomers in unequal abundances (Complexes 22–24, Table 5). The variable temperature spectra of the complex (X = Br) are illustrated in Fig. 7. The line assignments in the lowest temperature spectrum follow the methyl labelling in Fig. 6 and are based on careful comparisons with the corresponding homochalcogen complexes. On raising the temperature of the sample, the expected band broadenings and coalescences occurred as the rates of pyramidal inversion at the chalcogen atoms increased. We show later that this may be ascribed to inversion at sulphur and selenium atoms *trans* to the Pt–Me group. In the spectra shown in Fig. 7, sulphur inversion has become rapid at 32.8°C and both sulphur and selenium inversions are rapid at 131.8°C. Total band shape analyses were not preformed on the spectra of these mixed chalcogen ligand complexes since the spectral changes were predictably more complex than for the homochalcogen complexes and did not war-

Table 4. Arrhenius and Eyring parameters for sulphur inversion[a] in *cis*-[MX$_2$L] complexes

| No. | Solvent | $T_c{}^b$/K | $E_a$/kJ mol$^{-1}$ | $\log_{10} A$ | $\Delta H^\ddagger$/kJ mol$^{-1}$ | $\Delta S^\ddagger$/JK$^{-1}$ mol$^{-1}$ | $\Delta G^\ddagger$(298.15K)/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | $(CD_3)_2SO$ | 382 | 84.3 ± 0.5 | 13.3 ± 0.1 | 81.1 ± 0.5 | -0.9 ± 1.3 | 81.40 ± 0.11 |
| 2 | $(CD_3)_2SO$ | 361 | 77.2 ± 1.4 | 13.1 ± 0.2 | 74.3 ± 1.4 | -3.4 ± 4.1 | 75.25 ± 0.24 |
| 3 | $CD_3CN$ | 314<br>319$^c$ | 70.9 ± 0.9<br>73.1 ± 0.9 | 13.2 ± 0.2<br>13.5 ± 0.2 | 68.4 ± 0.9<br>70.5 ± 0.9 | -0.6 ± 3.0<br>5.5 ± 3.0 | 68.61 ± 0.01<br>68.82 ± 0.04 |
| 4 | $CD_3CN$ | 276<br>285$^c$ | 68.3 ± 1.1<br>66.3 ± 1.1 | 13.8 ± 0.2<br>13.4 ± 0.2 | 66.0 ± 1.1<br>63.9 ± 1.1 | 10.5 ± 4.0<br>4.2 ± 3.9 | 62.88 ± 0.08<br>62.76 ± 0.08 |
| 5 | $CDCl_3$ | 320 | 74.7 ± 1.8 | 13.4 ± 0.3 | 72.0 ± 1.8 | 2.4 ± 5.7 | 71.29 ± 0.13 |
| 7 | $CD_2Cl_2$ | 283 | | | | | 63.9 ± 0.5$^d$ |
| 8 | $(CD_3)_2SO$ | 295 | 68.8 ± 0.5 | 13.3 ± 0.1 | 66.3 ± 0.5 | 2.3 ± 1.6 | 65.61 ± 0.07 |
| 9 | $CD_3CN$ | 320 | 74.5 ± 0.6 | 13.5 ± 0.1 | 71.9 ± 0.6 | 5.7 ± 2.0 | 70.24 ± 0.01 |
| 10 | $CD_3CN$ | 293 | 72.0 ± 0.3 | 14.7 ± 0.05 | 69.7 ± 0.3 | 29.5 ± 1.0 | 60.88 ± 0.01 |
| 11 | $CD_3CN$ | 269<br>274$^c$ | 60.3 ± 0.3<br>60.7 ± 0.8 | 13.1 ± 0.1<br>13.2 ± 0.2 | 58.1 ± 0.3<br>58.4 ± 0.8 | -0.7 ± 1.3<br>0.5 ± 3.0 | 58.29 ± 0.01<br>58.28 ± 0.09 |
| 12 | $(CD_3)_2SO$ | 228<br>230$^c$ | 53.0 ± 0.5<br>52.9 ± 0.6 | 13.5 ± 0.1<br>13.5 ± 0.1 | 51.1 ± 0.5<br>51.0 ± 0.6 | 7.8 ± 0.2<br>7.3 ± 2.7 | 48.73 ± 0.15<br>48.78 ± 0.18 |
| 13 | $CD_2Cl_2$ | 269 | 66.0 ± 1.1 | 13.9 ± 0.2 | 63.8 ± 1.1 | 14.3 ± 4.1 | 59.50 ± 0.12 |
| 15 | $CD_2Cl_2$ | 228 | 51.1 ± 1.5 | 12.9 ± 0.3 | 49.1 ± 1.5 | -3.9 ± 6.5 | 50.3 ± 0.40 |

[a] Energy data derived from SMe region signals except where stated

[b] Coalescence temperature for SMe signals

[c] Coalescence temperature and associated energy data for olefinic proton signals

[d] Value based on a single fitting at 290.0 K

Table 5. Static parameters for the complexes [PtXMe{MeE(CH$_2$)$_2$E'Me}]

| Complex No | T/°C | Solvent | Meso(syn) isomer | | | | | | | DL(anti) isomer | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Pt-Me | | E-Me | | | | $p^d$ | Pt-Me | | E-Me | | | | $p^d$ |
| | | | $\nu^a$ | $^2J^b$ | ν(trans Me) | $^3J^c$ | ν(trans X) | $^3J$ | | ν | $^2J$ | ν(trans Me) | $^3J$ | ν(trans X) | $^3J$ | |
| 16 | -49.8 | $CD_2Cl_2$ | 62.9 | 71.9 | 262.9 | 18.2 | 261.6 | 74.0 | 0.33 | 70.1 | 71.4 | 238.6 | 19.0 | 248.0 | 73.1 | 0.67 |
| 17 | -62.0 | $CD_2Cl_2$ | 68.8 | 72.5 | 265.1 | 18.7 | 262.2 | 74.7 | n | 76.0 | 71.5 | 238.5 | 19.5 | 248.2 | 74.0 | n |
| 18 | -50.9 | $CD_2Cl_2$ | 79.8 | 73.0 | 266.8 | 20.5 | 262.0 | 71.8 | 0.31 | 87.2 | 72.5 | 238.3 | 21.0 | 244.6 | 71.3 | 0.69 |
| 19 | -3.2 | $CDCl_3$ | 82.5 | 70.8 | 250.2 | 15.1 | 248.3 | 59.8 | 0.43 | 90.1 | 70.6 | 230.2 | 15.6 | 237.3 | 59.1 | 0.57 |
| 20 | -1.5 | $CDCl_3$ | 87.9 | 71.5 | 250.0 | 15.9 | 250.0 | 60.1 | n | 95.5 | 71.0 | 230.2 | 16.1 | 237.8 | 59.8 | n |
| 21 | -1.5 | $CDCl_3$ | 100.1 | 73.0 | 252.4 | 16.6 | 250.2 | 61.0 | 0.39 | 107.2 | 72.5 | 230.2 | 17.1 | 235.6 | 56.6 | 0.61 |
| 22 | -62.3 | $CD_2Cl_2$ | 62.3$^e$<br>67.9$^e$ | 70.1<br>73.2 | 263.9<br>245.4 | 17.8<br>15.1 | 247.8<br>262.0 | 61.1<br>73.3 | 0.14<br>0.23 | 69.6<br>75.9 | 70.3<br>72.5 | 236.6<br>225.1 | 18.6<br>16.1 | 236.1<br>246.6 | 60.5<br>73.0 | 0.26<br>0.37 |
| 23 | -47.0 | $CD_2Cl_2$ | 70.3$^e$<br>75.0 | 70.6<br>73.4 | 266.2<br>245.5 | 18.3<br>15.5 | 249.0<br>262.0 | 61.9<br>72.9 | 0.14<br>0.24 | 77.1<br>83.0 | 70.3<br>72.5 | 237.2<br>224.7 | 19.8<br>15.9 | 235.8<br>245.5 | 61.0<br>72.5 | 0.25<br>0.37 |
| 24 | -62.0 | $CD_2Cl_2$ | 81.7$^e$<br>84.2$^e$ | 71.8<br>73.9 | 269.7<br>245.7 | n<br>15.3 | 263.1<br>262.0 | n<br>n | n<br>n | 88.5<br>92.8 | 71.9<br>73.2 | 236.7<br>223.4 | 19.8<br>17.1 | 243.5<br>243.5 | 71.3<br>n | n<br>n |

[a] Chemical shifts ν/Hz measured at 100 MHz relative to $Me_4Si$.

[b] $^2J$(Pt-C-H)/Hz

[c] $^3J$(Pt-E-C-H)/Hz

[d] Isomer populations

[e] In these mixed chalcogen ligand complexes there are two distinct syn(DL-1,4) isomers and two distinct anti(DL-2,3) isomers (Fig. 6).

n Not calculated

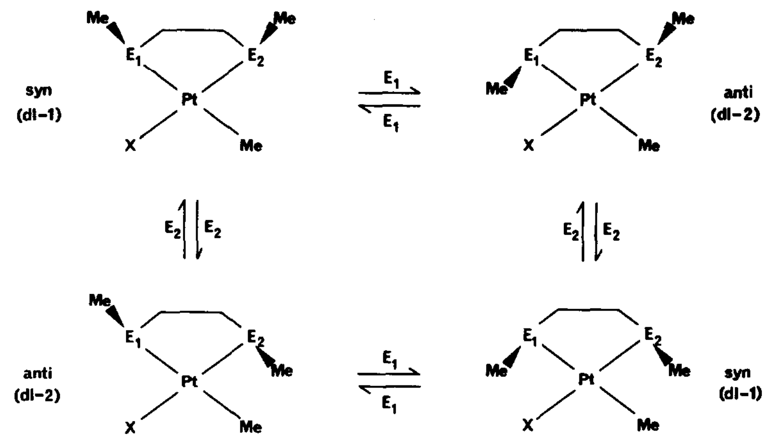


Fig. 5. Diastereoisomers of *cis*-[PtXMe{MeE(CH$_2$)$_2$EMe}] complexes showing the two possible E inversion pathways.

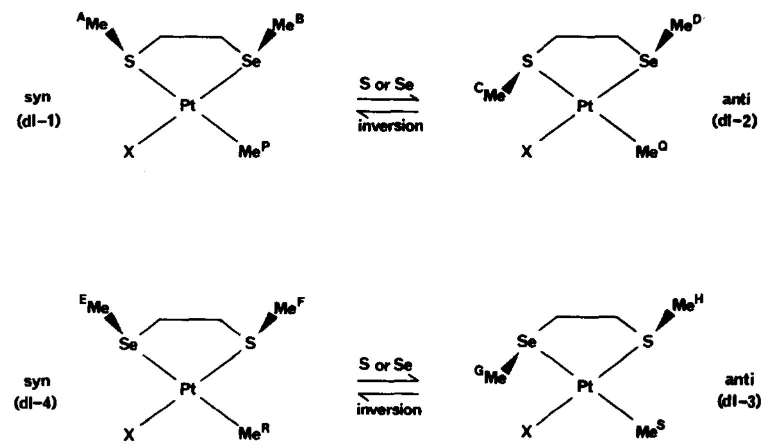


Fig. 6. Structural and diastereoisomers of [PtXMe{MeS(CH$_2$)$_2$SeMe}]. Only one of each DL pair is depicted.

Table 6. Energy parameters for the complexes [PtXMe{MeE(CH$_2$)$_2$Me}]

| Complex No. | Complex | $E_a$/kJ mol$^{-1}$ | $\log_{10} A$ | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$mol$^{-1}$ | $\Delta G^{\ddagger}$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 16 | [PtClMe{MeS(CH$_2$)$_2$SMe}] | 61.9 ± 3.9 | 13.2 ± 0.8 | 59.7 ± 3.9 | -0.2 ± 14.7 | 59.8 ± 0.5 |
| 18 | [PtIMe{MeS(CH$_2$)$_2$SMe}] | 60.3 ± 2.9 | 13.0 ± 0.6 | 58.1 ± 2.9 | -3.4 ± 11.2 | 59.2 ± 0.5 |
| 19 | [PtClMe{MeSe(CH$_2$)$_2$SeMe}] | 66.0 ± 3.8 | 12.0 ± 0.6 | 63.3 ± 3.8 | -24.6 ± 12.0 | 70.7 ± 0.2 |

rant the considerable computational efforts that would have been involved.

No further significant spectral changes were noted on heating these mixed chalcogen ligand complexes to their decomposition points. It thus appears that other fluxional rearrangements so characteristic of the Pt(IV) complexes of type [PtXMe$_3${MeE(CH$_2$)$_2$E'Me}][16] are absent in the Pt(II) complexes of type [PtXMeL].

## DISCUSSION

### *Static NMR parameters*

Considering first the [MX$_2$L] complexes (Table 3), the chemical shift assignments are based on the lower populated isomer being the *meso* form due to steric factors. On this assumption the SMe protons in this isomer appear at somewhat higher frequencies than their position in the DL isomer in most cases. A change in halogen

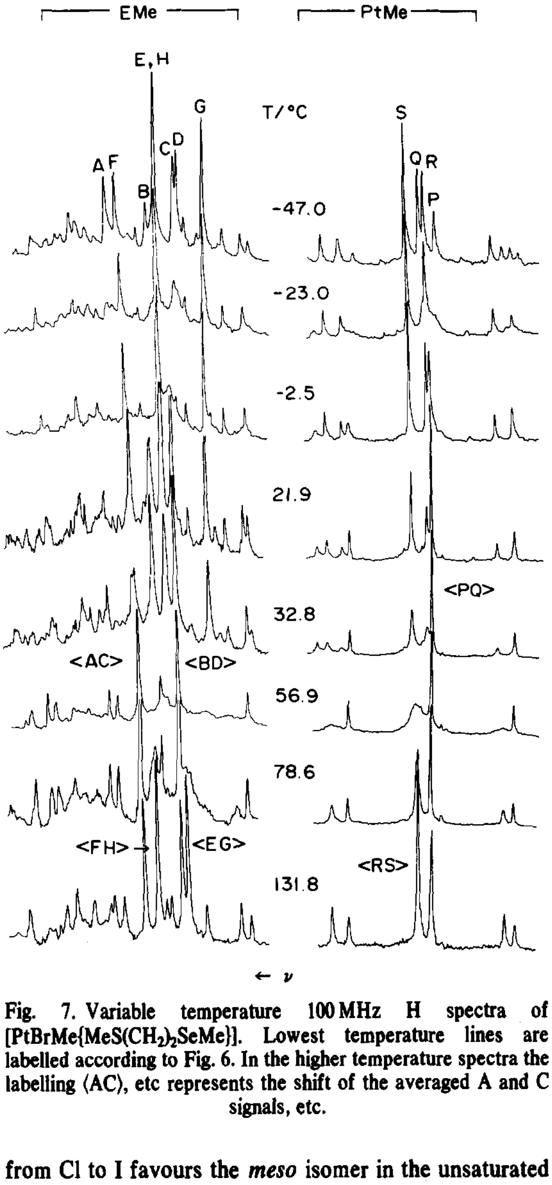


Fig. 7. Variable temperature 100 MHz H spectra of [PtBrMe{MeS$(CH_2)_2$SeMe}]. Lowest temperature lines are labelled according to Fig. 6. In the higher temperature spectra the labelling ⟨AC⟩, etc represents the shift of the averaged A and C signals, etc.

from Cl to I favours the *meso* isomer in the unsaturated ligand complexes but favours the DL form in the cases of saturated ligands. In all cases, however, sizeable high frequency shifts of the SMe protons occur. This is particularly apparent in the olefinic ligand complexes (Nos. 3, 4; 11, 12) where the DL isomer signals experience such large high frequency shifts that they occur at higher frequencies than the *meso* signals. The magnitude of the $^3$J (PtH) coupling constants are also halogen dependent, increasing with halogen size for the SMe protons and decreasing for the olefinic protons. The higher values of $^3$J(PtH) coupling for the olefinic protons (74–83 Hz) compared to the SMe protons (45–51 Hz) may be ascribed to the greater s character of the olefinic carbons compared to the methyl carbons.

In the case of the [PtMeXL] complexes, certain striking differences in the static parameters compared to those of $[PtX_2L]$ complexes are apparent. For instance, $^3$J(PtH) values for SMe protons *trans* to halogen lie in the range 56–75 Hz but, for these protons *trans* to methyl, values in the range 15–18 Hz were detected. This illustrates the large difference in the *trans* influence[24] of halogen and methyl groups. The $^2$J(PtMe) values in the range 70–74 Hz are somewhat lower than those predicted from results obtained for the mononuclear complexes $[PtMe_3X${MeE$(CH_2)_2$EMe}] in which the J values for Pt–Me *trans* to E–Me are of the order of 69–71 Hz. Now the magnitudes of coupling constants may, to a first approximation, often be related to the magnitude of the Fermi contact term, i.e. to the amount of *s* character in the bond. Oxidation from platinum(II) to platinum(IV) implies a change in hybridisation of platinum orbitals from $dsp^2$ to $sp^3d^2$ and a consequent reduction in the magnitude of $^2$J(PtMe) values in platinum(IV) complexes to two thirds their values in the corresponding platinum(II) complexes. The fact that this was not observed here suggests that the above simple theoretical model is inadequate in this case.

### *Pyramidal inversion energies*

These are listed in Tables 4 and 6. For the *cis*$[MX_2L]$ (L = homochalcogen ligands) complexes, only one pyramidal inversion pathway is possible (Fig. 1). For the *cis*-[PtXMeL] (L = MeE$(CH_2)_2$EMe) complexes (Fig. 5) the energies calculated are lower by *ca.* 15–20 kJ mol$^{-1}$ compared to the $[MX_2L]$ complexes and are therefore attributed to inversion of the chalcogen *trans* to the methyl group rather than that *trans* to the halogen. This lowering of energy again reflects the different *trans* influences of halogen and methyl groups.

No inversion energies were calculated for the *cis*-[PtMeX{MeS$(CH_2)_2$SeMe}] complexes for reasons mentioned earlier. The spectral changes, however, can be qualitatively interpreted to give a relative ordering of the various possible inversion pathways (Fig. 6). There are four such pathways depending on whether inversion involves S or Se atoms situated either *trans* to X or *trans* to methyl. We have shown in earlier work on platinum(IV) systems[15], that, in general, S inversion occurs more readily than Se inversion (the energy difference is *ca.* 10 kJ mol$^{-1}$). In the present work we have shown that the strong *trans* influence of Me lowers the S inversion barrier by *ca.* 15–20 kJ mol$^{-1}$. Moreover, a $\Delta G^{\ddagger}$ value of 70 kJ mol$^{-1}$ has been calculated for Se inversion *trans* to methyl (Complex No. 19) whereas inversion at Se *trans* to halogen, as in the complexes $[PtX_2${MeSe$(CH_2)_2$SeMe}], was too slow to be measured by DNMR methods. In the complex [PtXMe{MeS$(CH_2)_2$SeMe}] we can therefore predict that the relative order of inversion energies will be S(*trans* Me) (~60 kJ mol$^{-1}$) < Se(*trans* Me) (~70 kJ mol$^{-1}$ < S(*trans* X) (~75–80 kJ mol$^{-1}$) < Se(*trans* X) (~85–90 kJ mol$^{-1}$). The two coalescence phenomena at *ca.* 0° and 60°C observed in Fig. 7 can therefore be attributed with some certainty to inversion at S *trans* to methyl and at Se *trans* to methyl respectively.

(i) *Variation in metal.* The change of metal from Pt to Pd in the complexes $[MX_2L]$ produces a decrease in the S inversion barrier of 10–15 kJ mol$^{-1}$. This trend, which has been observed previously,[11–13] may be explained in terms of the greater strength of the Pt–S bond compared with the Pd–S bond.

(ii) *Variation in metal oxidation state.* Since we have shown that in the complexes [PtXMeL] pyramidal inversion occurs at chalcogens *trans* to Me, these systems are well suited for comparison with the trimethylplatinum(IV) complexes $[PtXMe_3${MeE$(CH_2)_2$EMe}][15]. Comparison of $\Delta G^{\ddagger}$ values of the appropriate complexes reveals a consistent increase of the chalcogen barrier of 1.5–4.5 kJ mol$^{-1}$ on going from platinum(II) to platinum(IV). This trend, which may be primarily associated with a slight increase in platinum-chalcogen bond strength on oxidation from platinum(II) to platinum(IV), parallels that found for the complexes $[PtX_2\{MeS(CH_2)_2SMe\}]$ and $[PtX_4\{MeS(CH_2)_2SMe\}]$.[25]

(iii) *Variation of halogen.* The effects of the difference in *trans* influence between halogens and methyl groups have been discussed already. The relative *trans* influences of the three halogens themselves are reflected in the energy data in Table 4 for the *cis*$[MX_2L]$ complexes. When M = Pt(II) the energy barriers ($\Delta G^{+}$ values) show a consistent decrease by 6–7 kJ mol$^{-1}$ from chloro to iodo complexes. When M = Pd(II) the decrease is by 9–10 kJ mol$^{-1}$. The relative order of $\Delta G^{+}$ values, namely $X = Cl > Br > I$ is in accord with increasing *trans* influence, and a concomitant weakening of the M–S bonds.

(iv) *Variation in ligand ring size.* A comparison of the $\Delta G^{\neq}$ values of $[PtCl_2\{MeS(CH_2)_2SMe\}]$ and $[PtCl_2\{MeS(CH_2)_3SMe\}]$ in Table 4 shows a large decrease of *ca.* 16 kJ mol$^{-1}$ as the heterocyclic ring increases from five to six members. This trend is in keeping with that found for inverting nitrogen atoms in various sized rings,[26] but differs somewhat from our earlier albeit not strictly analogous study[1] of the complexes *trans* $[MX_2\{\overline{S(C}R_2)_n\}_2]$ (M = Pd(II), Pt(II), $n$ = 2–5). Here sulphur inversion energies in the five and six-membered rings ($n$ = 4, 5) were virtually the same and essentially no different from those of open-chain sulphide complexes. It is of interest to note that in the platinum(IV) complexes,[15] increasing the ring size from five to six caused a lowering of $\Delta G^{+}$ of 5–6 kJ mol$^{-1}$.

(v) *Variation in ligand back-bone.* The effect of varying the ligand back-bone from aliphatic to aromatic to olefinic produced consistent trends in both platinum and palladium complexes. The change aliphatic → aromatic (e.g. complexes 1 → 5 or 9 → 13, Table 4) caused a lowering of the S inversion barrier of 10–11 kJ mol$^{-1}$, whereas the change aromatic → olefinic (e.g. complexes 5 → 3 or 13 → 11, Table 4) caused a further lowering of 1–2 kJ mol$^{-1}$. These decreases in barrier height are clear examples of $(3p–2p)\pi$ conjugation effects between the chalcogen lone pair and the ligand back-bone, such interactions being more effective in the planar transition state than in the pyramidal ground state. These effects have already been observed in the case of Group VA elements.[27] The results are consistent with those of Mislow *et al.*[28,29] for phosphorus and arsenic inversion. In the former case replacement of an alkyl by an aryl group in acyclic dialkylarylphosphines lowers the phosphorus inversion barrier by *ca.* 9 kJ mol$^{-1}$ due to $(3p–2p)\pi$ delocalisation.

Additional data supporting $(3p–2p)\pi$ conjugation effects have been obtained from appropriate complexes in the platinum(IV) series. For example, $\Delta G^{+}$ values for S inversion in the complexes $[PtClMe_3\{MeS(CH_2)_2SMe\}]$, $[PtClMe_3\{o\text{-}MeS(C_6H_4)SMe\}]$, and $[PtClMe_3\{MeSCH{=}CHSMe\}]$ are 63.3[15], 52.2[16] and 50.5[30] kJ mol$^{-1}$ respectively. Similar trends will also be reported in rhenium(I) carbonyl complexes.[31]

## FLUXIONAL REARRANGEMENTS

Since no further spectral changes occurred after pyramidal inversions became fast on the NMR time scale, it is apparent that the 180° ligand rotation movement ("pancake flip") we proposed for the mononuclear platinum(IV) complexes is *not* taking place in these platinum(II) complexes. Such a movement would only be observable in the [PtXMeL] complexes by virtue of their lower symmetry compared to the $[MX_2L]$ complexes. Its absence, however, in these former complexes in the temperature range studied calls for some explanation. In the Pt$^{IV}$ complexes it would appear that the "pancake flip" mechanism requires inversion at *both* chalcogen atoms to be rapid in NMR terms before the fluxion can operate. In the complexes $[PtXMe\{MeE(CH_2)_2E'Me\}]$ (E = E′ and E = S, E′ = Se) the "pancake flip" mechanism would be expected to interchange the resonances due to EMe(*trans* X) and EMe(*trans* Me). In the particular case of $[PtBrMe\{MeS(CH_2)_2SeMe\}]$, for example, (Fig. 7), the fluxion would interconvert the two geometrical isomers and so produce averagings of the inversion-averaged S-methyls ⟨AC⟩ and ⟨FH⟩, the Se-methyls ⟨BD⟩ and ⟨EG⟩, and the Pt-methyls ⟨PQ⟩ and ⟨RS⟩. This was *not* observed at temperatures below decomposition, which suggests that the inversions at either or both E atoms *trans* to X (most likely Se *trans* X) were too slow to initiate the "pancake flipping".

The nature of the transient intermediates almost certainly has a strong influence on the ease of the fluxional motion. For platinum(II) complexes, the motion will involve a change from four to pseudo-six coordination at the metal, whereas the corresponding mechanism for platinum(IV) complexes requires a change in coordination number from six to pseudo-eight. This a proportionally smaller change in coordination but almost certainly other factors concerning the stabilities of the ground and transition states of these species will be important in finally determining the ease of the fluxional rearrangements in these complexes.

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